NON-MANDATORY APPENDIX -

APPENDIX III: OXIDATION AND ITS EFFECTS ON GRAPHITE

A3-1000 INTRODUCTION

Over the lifetime of the graphite core structure in a reactor, the graphite components may be progressively oxidised either by the coolant itself, or by impurities in the coolant. The former is the case when the coolant is carbon dioxide (CO_2), and the latter is the case when the coolant in helium (He).

Since oxidation generally has a detrimental effect on some properties of the graphite, most importantly strength, it is therefore necessary to be able to predict the level of oxidation to be expected in individual components through life (due to the coolant), or under accident conditions (due to air ingress). The effect that oxidation has on strength, and other properties, will have an impact on the integrity and hence lifetime of individual components.

A3-1100 SCOPE

This Appendix describes the different graphite moderated, gas-cooled reactor designs; the oxidation mechanisms of importance; the way they relate to the different reactor designs; the current models used to calculate the amount of graphite oxidation that occurs; the data required for each model; and the effects of oxidation on graphite properties and hence on graphite component integrity and lifetime.

A3-2000 REACTOR DESIGNS

Gas-cooled reactor designs can be placed in two basic categories, namely He cooled and CO_2 cooled. An important distinction is the temperature of the graphite during normal operation as this dictates the main oxidation mechanism.

In the He cooled reactors, almost all of the graphite is at a temperature above 500^{o}C during normal operation, and are referred to as High Temperature Reactors (HTRs). The oxidation of the graphite is almost entirely thermal oxidation, with a much lower amount of radiolytic oxidation.

In the CO_2 cooled reactors, the oxidation of the graphite is almost entirely radiolytic oxidation, as the temperature of the graphite in the core never exceeds 500^{o}C during normal operation, with the result that thermal oxidation is negligible. Significant radiolytic oxidation occurs in all the AGRs, and in the last two Magnox stations built (but these are approaching the end of their lives). For this Appendix, therefore, only the AGRs are considered.

A3-2100 HELIUM COOLED

There are basically two types of He cooled HTR design, namely the pebble bed type and the prismatic type.

A3-2110 PEBBLE BED TYPE

Although pebble bed type reactors have been built in the past (in Germany) there are no reactors of this type currently in operation. However, a new design is being developed and this is the Pebble Bed Modular Reactor (PBMR). This is therefore the design used in the remainder of this Appendix to cover pebble bed type reactors.

A vertical section through the reactor is shown in Fig A3-1, and a horizontal section in Fig A3-2. It uses fuel in the form of a spherical pebble (60 mm in diameter), and has a fixed outer side reflector and inner reflector which together form an annulus through which the fuel pebbles flow.

The outer side reflector and inner reflector are formed from a large number of graphite blocks which are interconnected using rectangular shaped keys and cylindrical shaped dowels. These structures are supported by the bottom reflector. The top reflector is suspended .

The coolant flow returning from the main power system passes into a lower plenum in the bottom reflector and flows upwards through a number of riser channels in the outer side reflector blocks, before exiting via a plenum above the pebble bed. The flow then passes downwards over the fuel pebbles before exiting through channels in the bottom reflector.

A3-2120 PRISMATIC TYPE

Prismatic type reactors have been built in the past (in the US and UK), and there is currently a prototype reactor in operation in Japan. There are also new designs being developed. These include the ANTARES reactor (France) and the Gas-turbine Modular Helium Reactor (US/Russia). The ANTARES design is used in the remainder of this Appendix to cover prismatic type reactors.

A vertical section through the reactor is shown in Fig A3-3, and a horizontal section in Fig A3-4. A typical fuel block is hexagonal in shape and contains a large number of vertical holes, as shown in Fig A3-5. Some of the holes are full height, but the others are blind ended. The fuel is in the form of cylindrical compacts which are located in the blind ended holes. The full height holes provide passage for the coolant flow.

The active core is formed by columns of these fuel bricks. The active core is surrounded by the side reflector, which is made up of hexagonal blocks with holes for coolant flow. These structures are supported by the bottom reflector and are surmounted by the top reflector.

The coolant flow returning from the ??? passes……..

A3-2200 CARBON DIOXIDE COOLED

There are four basic AGR core designs but they are all similar enough in terms of construction and coolant flow paths for the purposes of this Appendix.

A vertical section through the reactor is shown in Fig A3-6, and a horizontal section in Fig A3-7. An isometric shown the arrangement of blocks and keys is shown in Fig A3-8. A typical fuel block is octagonal in shape and contains a large number of vertical holes, referred to as methane diffusion holes.

The active core is formed by columns of fuel blocks (which provide continuous passage for the fuel stringers) interspaced with columns of square blocks (which provide continuous passage for control rods, other devices, or coolant flow). The active core is surrounded by the side reflector, which is made up of octagonal blocks with holes for coolant flow. These structures are supported by the bottom reflector and are surmounted by the top reflector.

The typical coolant flow paths for an AGR are illustrated in Fig A3-9. The flow exiting the circulators splits into two flows referred to as the by-pass and re-entrant flows. The by-pass flow enters to core through the bottom core support structure. The re-entrant flow passes up the outside of the core and enters the top of the core through the gaps between the blocks forming the top reflector. The coolant flows down through arrow head shaped passages between the blocks and also down through the methane diffusion holes. The by-pass and re-entrant flows combine in a plenum in the bottom reflector before entering the fuel channel, where it then enters the bottom of the fuel stringer.

A3-3000 OXIDATION MECHANISMS

A3-3100 THERMAL OXIDATION

There are two types of thermal oxidation that are important to graphite core designs. One is the long term oxidation of the graphite by the impurities in the coolant, which occurs at a very slow rate, but could nevertheless result in a significant oxidation level over the operating life of the plant. The second is the rapid oxidation that would occur during an air ingress event, or a steam ingress event.

A3-3110 NORMAL OPERATION

A3-3150 ACCIDENT CONDITIONS

A3-3200 RADIOLYTIC OXIDATION

Radiolytic oxidation of graphite in a CO_2 environment occurs within the open pore structure of the graphite. Irradiation of the graphite results in the generation of highly energetic oxidising species in the gas phase within the open pores. Gasification of a carbon atom at a pore surface occurs once the oxidising species reaches the pore surface. However, the diffusion of the species to the surface is affected by the presence of carbon monoxide (CO) and methane (CH_4), as it can react with these molecules and become deactivated.

The presence of CH_4 results in further inhibition of the oxidation rate by a process that is assumed to work by either interfering with the surface chemistry, or by depositing sacrificial carbon on the pore surface due to radiolytic breakdown of the CH_4. (The methane diffusion holes were included in the blocks to supplement the methane entering via the outer surfaces)

Graphite oxidation and methane destruction are represented by the equations:

$C + CO_2 \rightarrow 2CO$ (Rate = K_1)

$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O$ (Rate = K_2)

[K_1 is derived from the rate of removal of graphitic carbon. K_2 is calculated using an empirical expression for the methane destruction rate G(-CH)].

A3-4000 METHODOLOGY

A3-4100 THERMAL OXIDATION

A3-4110 NORMAL OPERATION

A3-4150 ACCIDENT CONDITIONS

A3-4200 RADIOLYTIC OXIDATION

The amount of radiolytic oxidation that occurs in the AGRs is termed 'weight loss' and is normally expressed as a percentage of material lost.

The UK model for the AGR is based on the assumption that the local weight loss

Basically the calculation involves the 2D or 3D calculation of the coolant composition in the piece of graphite by solving the equations for gas transport, methane destruction and CO production

A3-3000 DATA

A3-3100 THERMAL OXIDATION

A3-3110 NORMAL OPERATION

The calculation of the thermal oxidation of a component with time during normal operation requires the following information:

A3-3150 ACCIDENT CONDITIONS

The calculation of the thermal oxidation of a component with time during accident conditions requires the following information:

A3-3200 RADIOLYTIC OXIDATION

The calculation of the radiolytic oxidation of a component with time during normal operation requires the following information.

A3-5000 EFFECT ON PROPERTIES

The important graphite properties that are affected by oxidation are strength, Young's modulus and …… It is important to note that the change in strength with oxidation is different for thermal oxidation compared to radiolytic oxidation. This is primarily because thermal oxidation affects the binder material more than radiolytic oxidation. The typical effect on properties are given below

A3-5100 STRENGTH

Oxidation always reduces strength. For relatively low weight losses (<5%), the reduction in strength is approximately linear as illustrated in Fig A3-?.

At higher weight losses (>5%), the reduction in strength can generally be represented as an exponential of the form:

$W(x) = A. e^{(-\lambda.x)}$

Where

W(X) = fractional reduction in strength

A is a constant

λ is a constant

x is the fractional weight loss (%/100)

Typical curves for thermal and radiolytic weight loss are also shown in Fig A3-?

The data used to determine the variation in strength with oxidation for a particular graphite will shown some scatter. For design purposes, it is necessary this variability be taken into account in the appropriate manner.

A3-4200 YOUNG'S MODULUS

Oxidation always reduces Young's modulus. As for strength, for relatively low weight losses (<5%), the reduction in Young's modulus (YM) is approximately linear as illustrated in Fig A3-?.

As for strength, for higher weight losses (>5%), the reduction in YM can generally be represented as an exponential of the form:

$W(x) = A. e^{(-\lambda.x)}$

Where

W(X) = fractional reduction in YM

A is a constant

λ is a constant

x is the fractional weight loss (%/100)

Typical curves for thermal and radiolytic weight loss are also shown in Fig A3-?

The data used to determine the variation in YM with oxidation for a particular graphite will shown some scatter. For design purposes, it is necessary this variability be taken into account in the appropriate manner.

There is benefit in having a model that can perform calculations with a coolant composition that varies with time.

Table 1 –

Table 2 –

Figure 1 – Vertical section through a pebble bed type reactor (PBMR)

Figure 2 –Horizontal section through a pebble bed type reactor (PBMR)

Figure 3 – Vertical section through a prismatic type reactor (ANTARES)

Figure 4 – Horizontal section through a prismatic type reactor (ANTARES)

Figure 5 – Vertical section through an AGR

Figure 6 – Horizontal section through an AGR

Figure 7– Block arrangement for an AGR

Figure 8 – Typical coolant flow paths for an AGR

Figure 9 –